Synopsis Of Proposed Thesis

Synthesis Of Diazafluorene and Benzimidazole anologs and their evaluation as an organocatalyst for CO_2 reduction

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Title: Synthesis of diazafluorene and Benzimidazole anologs and their evaluation as an organocatalysts for CO_2 reduction.

Introduction:

Carbon dioxide (CO_2) is the most abundant greenhouse gas in the atmosphere obtained from living and nonliving sources. From the last few years percentage of CO_2 in atmosphere is significantly increased.[1] The great efforts are required to develop technologies towards the reduction of CO_2 emission and its utilization. The CO_2 is a nontoxic, ubiquitous, economical and sustainable C_1 resource and it is being used as a chemical feedstock to prepare useful products such as urea, methanol, lactones, carboxylated structures, various heterocycles, biodegradable polymers, and polycarbonates. Such industrial applications would result in the consumption of ~116 million tons of CO_2 per year.

Among the numerous applications in organic synthesis, CO_2 can be applied as a desirable raw material for fuel production such as methanol.[2] However, CO_2 activation necessary for its chemical transformation is difficult due to a high thermodynamic and kinetic stability. Thus, a harsh condition e.g. as high reaction temperature/pressure are required for the transformation of CO_2 into useful chemicals. The use of organocatalysts in this CO_2 transformation has gained attention due to their nontoxic nature, stability along the reaction and resistant towards moisture. The cost-effectiveness, metal-free conditions and sustainability are the primary advantages of organic molecules. The CO_2 can be reduced either chemically using the 4-methyl-4,5-diazafluorene (**1**)[3] and the imidazole based radical (**2**)[4,5] or electrochemically using N,N-disubstituted benzimidazole (**3**)[6] to produce methanol (**see Figure 1**).

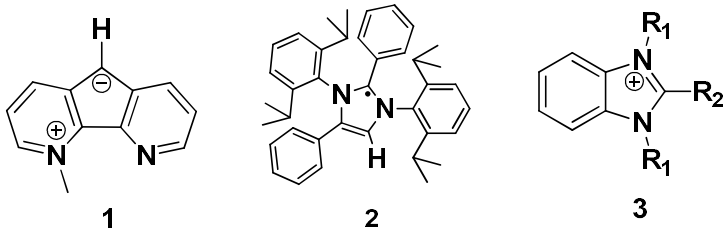


Figure 1: The 4-methyl-4,5-diazafluorene (**1**) , imidazole based radical (**2**) and N,N-disubstituted benzimidazole (**3**) used for CO_2 transformations and other applications.

The **1** and its anologues are the promising organocatalyst, those activate CO_2 by nucleophilic attack of negatively charged carbon of the organocatalysts. A stronger nucleophilic character of negatively charged carbon leads to a facile CO_2 activation and decreases ΔG of this step. Song *et. al*[7] shown that the mode of CO_2 activation by the actor diazafluorenide ligand can be tuned by varying the spectator metal center (**Figure 2**), this motivated to design the organocatalyst **1**. However, use of 1 in CO_2 reduction is limited due to the positive Gibbs free energy of the carboxylated product of CO_2 insertion. To overcome this organocatalyst 6 as well as 7 and its derivatives are synthesized (**Figure 3**), which shows improved performance.

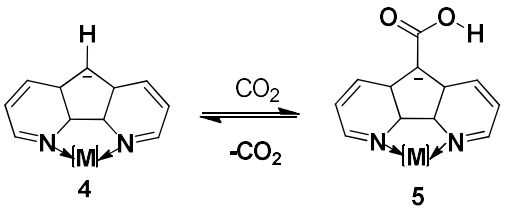


Figure 2: Carboxylation and decarboxylation using diazafluorenide ligand.

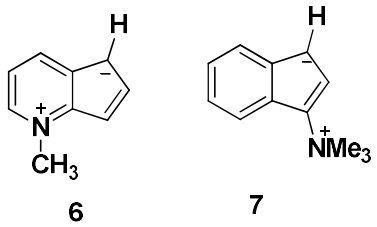
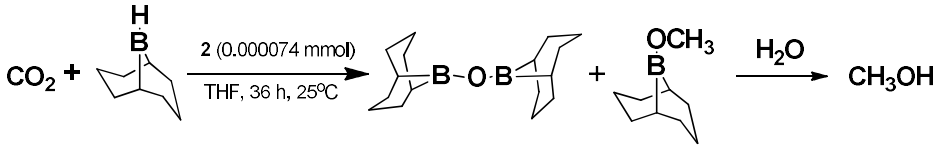


Figure 3: Diazafluorene as organocatalysts used for CO_2 reduction

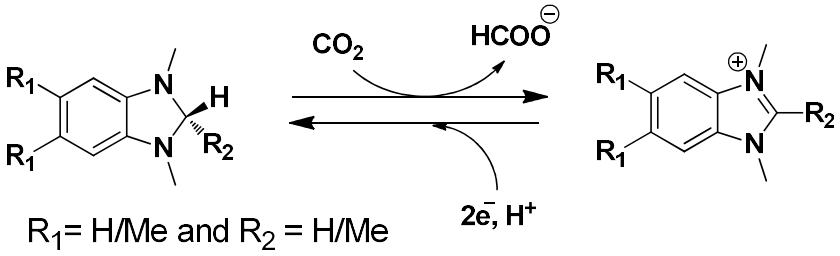
The reducing agent like hydroboranes/borohydride salts are used in presence of organocatalysts **1**, **2**, **6**, and **7** for the transformation of CO_2 into methanol (**Scheme 1**).



Scheme 1: Reduction of CO_2 using **1**/**2**.

On the other hand reduction of CO_2 using **2**, **3** and their analogues via hydride (H^-)

transfer(s) stands as one of the most promising approaches to convert CO_2 to methanol via formate. Although the many transition-metal-catalysts effectively reduce CO_2 to formate (and beyond), the high cost of homogeneous noble-metal catalysts effectively hampers the development of economical processes and also their selectivity is often limited due to formation of CO and/or H_2 in addition to formate. Murphy et al. recently proposed the role of an in situ generated C-2 protonated benzimidazole radical as a super electron donor performing a number of catalytic reactions. Still lot of work has to do regarding the benzimidazole radicals (**2**). So we want to go further and study the different derivatives and effect of substituents in this system.Mandal *et.al*[8] has prepared the first structurally characterized imidazole-based radical **2**, which reduces CO_2 to methoxyborane using 9-borabicyclononane (9-BBN) with highest TON value of 7550[9] Chern-Hooi Lim and co-workers have electrochemically transformed benzimidazolium cation to corresponding organo-hydride with quantitative yield and shown that electrochemically generated recyclable organo-hydrides are capable of transferring a hydride to CO_2.



The Quantum Mechanical (QM) calculations using Density Function Theory (DFT) have been performed to understand the reactivity **1-3** and their mechanism of CO_2 reduction. In **1** and its analogues (**6**,**7**) the CO_2 activation is governed by the nucleophilicity of the C9 in **1** and equivalent carbon centres in **6**/**7**. Furthermore the DFT calculations suggest that aromaticity of these catalysts is also useful indicator.

Review of Literature:

1.International status:

1.M. Izadyar *et. al*[10] made theoretical study performed on the mechanism aspects of the carbon dioxide conversion to methanol by using Proton sponge as a new efficient catalyst.

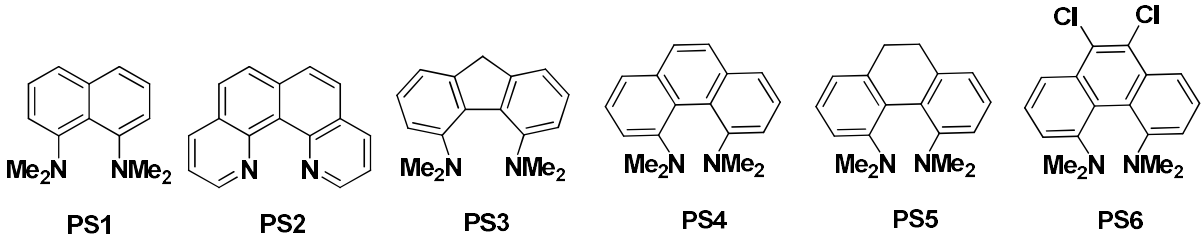
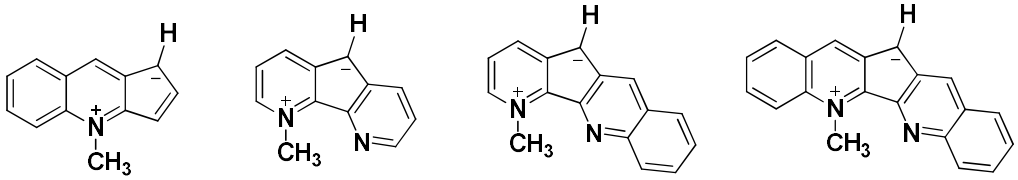


Figure 4: Structure of different Proton Sponge molecules

2.M. Izadyar *et al*[11] used borohydride salt for transformation of CO_2 into methanol. In this research catecholborane acts as the reducing agent in the presence of organocatalysts 1-4



1 2 3 4

3.Song *et al*[12] reported two carbon-center catalysts for CO_2 reduction to methanol.

4. Borohydride salts as high efficiency reducing reagents for carbon dioxide transformation to methanol. Hossein Sabet-Sarvestani, Hossein Eshghi Mohammad gives theoretical approach. Mohammad *et al*[10] studied the mechanism of CO_2 reduction to methanol using the borohydride salts of $M[RBH_3]$ as the reduction reagents, theoretically. A theoretical study has been performed on the mechanism aspects of the carbon dioxide conversion to methanol. The performance of four borohydride salts was also investigated in the gas and solvent phases theoretically. Based on the obtained data, solvent has remarkable effects on the rate determining step of the reaction. The steps of the overall reaction have been classified into three phases which two phases affected by the substituted groups of the borohydride salts. The electronic interactions and charge density of the boron atom affect the Gibbs free energy of activations during these processes. Finally, $Li[MeBH_3]$ and $Li[PhBH_3]$ have been proposed as the best reductive agents for this reaction.

5. Tuning the Reactivity of an Actor Ligand for Tandem Carbon dioxide and C−H Activations: From Spectator Metals to Metal-Free Vincent T. Annibale *et. al*[12] (University of Toronto, Canada), $M_5S_3H_6$. Song *et al* shown that the mode of CO_2 activation by the actor diazafluorenide ligand can be tuned by varying the spectator metal center. A RT reversible formal insertion of CO_2 into a remote ligand C−H bond was studied where the spectator metal's role is likely to modulate the strength of the resulting C−C bond and adjust the acidity of the C−H bond to allow the carboxylation and decarboxylation to occur readily at RT. Tuning the metal via oxidation state (e.g., Rh III vs Rh I) gave markedly different results in ligand-based reactivity Current efforts are focused on catalytic applications of this ligand-based and metal-free reactivity as well as establishing the scale of the electronic effects of various spectator metal centers.

6. Organocatalysts with carbon-centered activity for CO_2 reduction with boranes, Yanxin Yang, Maotong Xu, and Datong Song.

Datong *et al* reported two organocatalysts for CO_2 hydroboration to methylborylethers[13]which upon hydrolysis can produce methanol. These organocatalysts feature carbon- centered reversible CO_2 binding, broad borane scopes, and high catalytic activities. Datong demonstrated compounds 1 and 2 which not only bind CO_2 reversibly via the formal insertion of CO_2 into a C–H bond of the C5 ring, but also catalyze the hydroboration of CO_2 to methylborylethers which upon hydrolysis can produce methanol. These air and moisture-stable compounds that consist of only carbon, hydrogen, and nitrogen are the first catalysts with carbon centered activity for the reduction of CO_2 to methylborylethers. These catalysts feature broad borane scope and their catalytic activities are comparable to the best organocatalysts with heteroatom-based activity. The mechanism of the catalytic reactions are currently being investigated via experimental and computational methods.

7. Conversion of Carbon Dioxide into Methanol with Silanes over N-Heterocyclic Carbene Catalysts Siti Nurhanna Riduan, Yugen Zhang, and Jackie Y. Ying. Ying *et al*[14] reported the first N-heterocyclic carbene catalyzed reduction of CO_2 with silane under ambient conditions. Compared to transition-metal catalysts, NHCs present superior efficiency and are amenable to milder, less stringent reaction conditions. The catalytic reduction of CO_2 by NHCs also produces the methoxide product selectively in excess of 90 % hydrogen-transfer yield with gaseous CO_2 or dry air as the feedstock. This approach offers a very promising protocol for chemical CO_2 activation and fixation.

8. Photocyclisation of stilbene has been reported by Mallory *et al*[15.] in 1964 Columbia university, Newyork uses air and catalytic amount of I_2 to effect the oxidation. 'The early age' of reaction was reviewed by Mallory[16] in 1984 in huge chapter in the organic reaction series.

9. A theoretical investigation of substituent effects on the stability and reactivity of N-heterocyclic olefin carboxylates Liang Dong.

Liang Dong[17]studied the effect of substituents on the stability of NHO–CO_2 adducts and the reactivity of free NHOs theoretically by the combination of DFT calculations, MESP, and global nucleophilicity index analysis. . The nucleophilicity index analysis confirms that free NHOs are stronger nucleophiles than NHO–CO_2 adducts. Hence, the thermodynamically and kinetically unstable NHO–CO_2 adducts should be more efficient organocatalysts for nucleophile promoted reaction. The stability of NHO–CO_2 adducts as well as the reactivity of free NHOs are significantly influenced by the C- and N-substituents. The C-substituent exerts an electronic effect only. The electron-withdrawing C-substituent decreases the electron density on the carboxyl moiety of NHO–CO_2 and the terminal carbon atom of olefins, which favors decarboxylation but weakens the nucleophilicity of NHO. The N-substituent contributes both electronic and steric effects. As the steric bulk of the N-alkyl group increases, the stability of the NHO–CO_2 adduct and the reactivity of free NHO slightly increases. The balance between the stability of NHO–CO_2 adducts and the reactivity of free NHOs can be tuned by the combined effect of C- and N-substituents. NHO–CO_2 adducts with a weak electron-withdrawing group (unsaturated hydrocarbon moieties or -Ph) at the C-position, and a bulk aromatic substituent or ring strain at the N-position, are predicted to result in a more efficient catalyst for the carboxylative cyclization of propargylic alcohols with CO_2.

2.National status:

1.Assessment of Stereoelectronic Factors That Influence the CO_2 Fixation Ability of N-Heterocyclic Carbenes: A DFT Study Manjaly J. Ajitha and Cherumuttathu H. Suresh studied the CO_2 fixation ability of N-heterocyclic carbenes (NHC) assessed on the basis of electronic and steric properties of the N- and C-substituents, measured in terms of molecular electrostatic potential minimum, observed at the carbene lone pair region of NHC (Vmin1) as well as at the carboxylate region of the NHC−CO_2 adduct(Vmin2). BothVmin1andVmin2are found to be simple and efficient descriptors of the stereoelectronic effect of NHCs. The Vmin-based analysis also proved that the stereoelectronic effect of N- and C-substituents is additive. When only C-substituents are present in NHC, its CO_2 affinity solely depends on the

electronic effect, whereas if the N-center bears the substituents, the steric factor plays a major role in the carboxylation/decarboxylation process. For standard substituents, maximum CO_2 binding energy of 18.0 kcal/mol is observed for the most electrondonating combination of NMe_2 as the C-substituent and Me as the N-substituent. In this study, Suresh *et al* have used topological features of MESP to evaluate the stereoelectronic properties of NHC as well as the NHC−CO_2 adduct. In addition, the use of an N-substituent such as CH_2OH, $CH_2NHCOMe$, and CH_2NHPh substantially improve the CO_2 fixing ability of NHCs.

2.Photocyclisation of stilbene[18] done by Talele Harish R . an improved method has been reported for photocyclisation of stilbene to construct phenanthrene. Reaction is promoted by iodine while tetrahydrofuran is used as efficient and inexpensive scavenger of hydroiodic acid produce photocyclisation sequence . In another process cyclohexene is used as reagent for dehydrogenation step in place of THF / I_2.

Objectives:

- Analogs are used as an organocatalyst for CO_2 reduction.
- This is useful in the fuel production, oxidation of simple substrate, C-H functionalisation
- Photoelectrochemical cells used in construction of C-N , C-O , C-P bond.
- This result is environmently friendly and energy saving.
- It has high atom economy, low cost, lesser waste generation and green technology under mild condition.
- Electro& photochemical method give new & efficient access to radical ion charge transfer complex.
- PEC provide versatile & powerful approach to assembly of various heterocyclic structure.

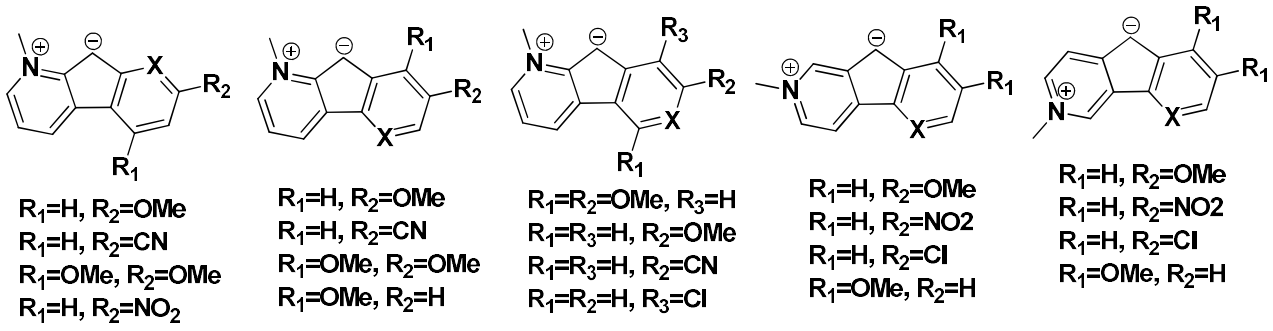
Importance of study:

We expoited novel, facial & tactic synthesis of 4,5-diazafluorene & benzimidazole. It act as organocatalyst in CO_2 reduction. The formation of this catalyst is ecofriendly, having low cost. This method is metal free. This organocatalyst is helpful in carbondioxide capture, fixation & activation by using N- heterocyclic carbene. In last two decade CO_2 emission caused a lot of environmental problems. In this research, homogeneous reaction & corresponding reaction mechanism devoted to the activation, capture & fixation of CO_2 by using NHC & related complexes will studied. The rational synthesis of organic compound is one of the primary goals of green & sustainable chemistry. In this we have underlined the current status of photoelectrochemistry to drive the synthesis of organic compound.

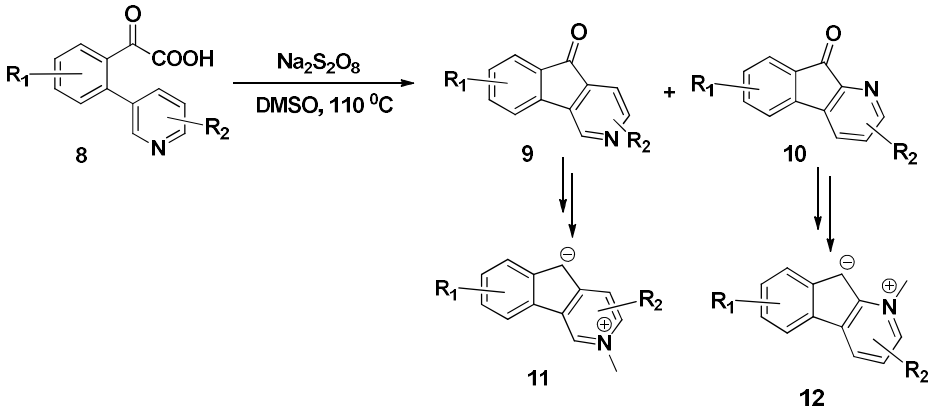
<u>Proposed Work Plan:</u>

I) Synthesis of azafluorene and diazafluorene analogues

In the earlier studies, scientists studied only simple 4,5-diazafluorene molecule, both with and without metals, for CO_2 reduction and C-H activation as discussed above. However, there no attempts on the systematic study of the substitution effect on **1**. Moreover the systematic understanding of the structural activity relationship for CO_2 activation has yet to be performed. Thus we propose to synthesize new diazafluorene, aryl azafluorene analogs and utilize them for CO_2 reduction, transformation and C-H activation. Here we will also study the effect of electron donating and electron withdrawing groups, different rings attached to diazafluorene on the CO_2 activation. Some azafluorene and diazafluorene molecules which will be synthesized and to be studied for CO_2 reduction are shown in **Figure 4**

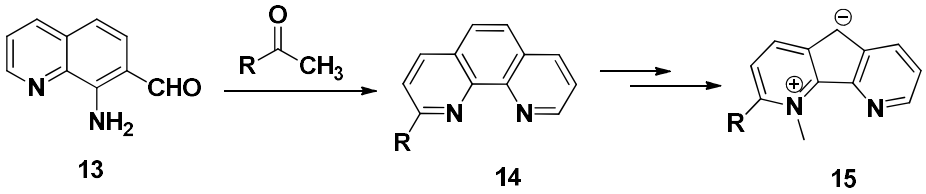


We will be investigating the azafluorene molecules with change in position of Nitrogen atom. These substituted monoazafluorenide may also be prepared by the treatment of substituted 2-oxo-2-(2-(pyridin-3-yl)phenyl)acetic acid (**8)** with oxidant ($Na_2S_2O_8$) to produces cyclised 5H-indeno[1,2-c]pyridin-5-one (**9)** and 9H-indeno[2,1-b]pyridin-9-one (**10).**[19] We want to transfer product **9** and **10** in to corresponding substituted monoazafluorenides **11** and **12** by sequence of the reactions (reduction, methylation and finally dehydrogenation, **Scheme 2**).



Scheme 2: Synthesis of substituted monoazafluorenide

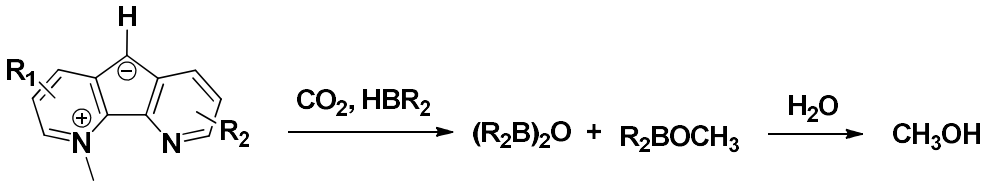
Condensation of 8-aminoquinoline-7-carbaldehyde **(13)** with ketone gives C-2 substituted 1,10-phenanthroline (**14**) which can be further converted to 2-subtituted N-methyl diazafluorenide (**15, Scheme3)**.



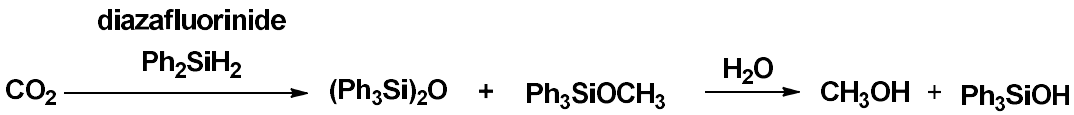
Scheme 3: Synthesis of 1,2-disubtituted diazafluorenide

Transformation of CO_2 to methanol using diazafluorene analogues

After preparation of substituted mono and diazafluorenides, these are used for the CO_2 reduction and transformation in presence of hydroboranes (HBR_2 = HBcat (catecholborane), HBpin (pinacolborane), 9-BBN (9-borabicyclo[3.3.1]nonane), $BH_3 \cdot SMe_2$ and $BH_3 \cdot THF$) to generate CH_3OBR_2 or $(CH_3OBO)_3$, products that can be readily hydrolyzed to methanol (**Scheme 4**).[20] The reduction can be achieved using mild reducing agents such as silanes (**Scheme 5**).[21]



Scheme 4: Reduction of CO_2 using organocatalysts in presence of hydroboranes

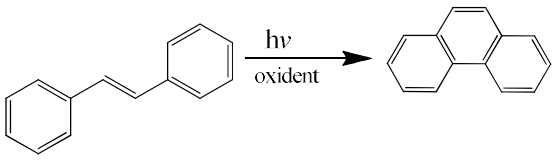


Scheme 5: Reduction of CO_2 using organocatalysts in presence of Silanes.

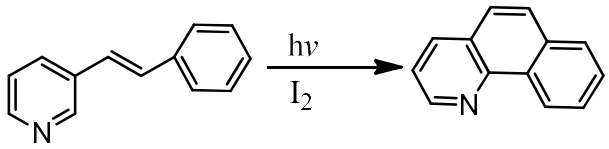
Furthermore epoxides and polyhydroxy compounds can be used for the transformation of CO_2 in to methanol. we will try different reducing reagents for the transformation of CO_2 into methanol using organocatalysts i.e. diazafluorenide.

II) Photocyclization of Stilbene:

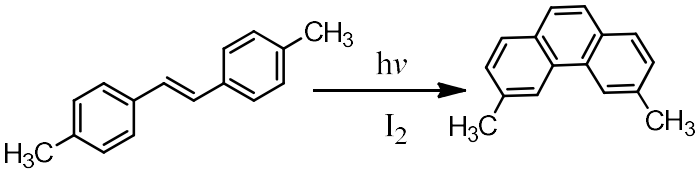
Photochemical isomerisation of double bond in stilbene has been extensively studied. From synthetic point of view the cis/ trans isomerisation occure rapidly under the reaction condition in such a way that different composition of cis/ trans stilbene give same product.



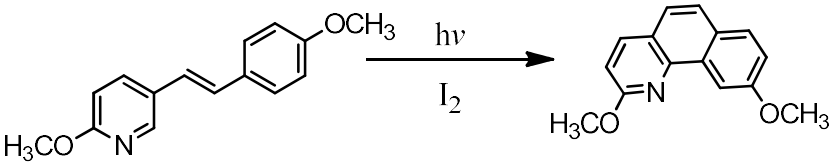
In earlier studies scientist studied only simple photocyclization of stilbene[22], but we will plan the study of N-containing stilbene photocyclization for the preparation of phenanthrene. Still the N- containing stilbene photocyclization was not reported. (**Scheme 6**).



p,p'-dimethyl stilbene is irradiated in presence of Iodine it undergo cyclisation[23.] Here Iodine is superb quencher.



We done photocyclization of substituted stilbene having electron donating and electron withdrawing group for the formation of N-containing subtituted phenanthrene.



III) Synthesis of benzimidazole analogues

In the past studies, scientists studied only simple benzimidazole molecule, both with and without metals for CO_2 reduction. However, there no attempts on the systematic study of the substitution effect on the analogs. Moreover the systematic understanding of the structural activity relationship for CO_2 activation has yet to be performed. So we want to synthesize different analogs of imidazole molecules or/and radical as shown in figure below[24]

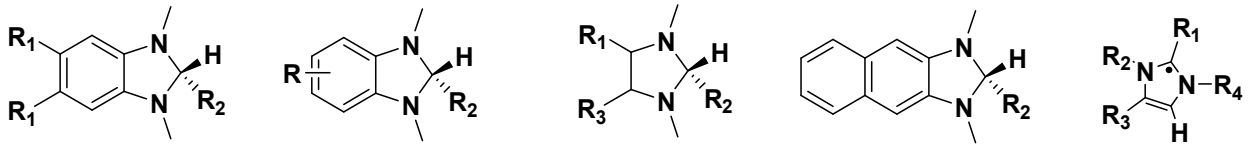
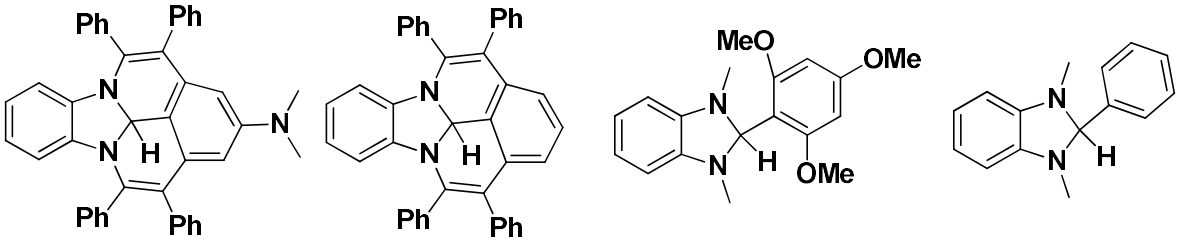
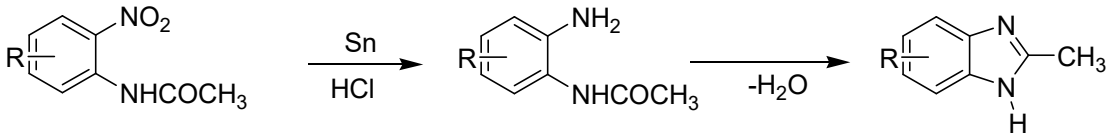


Figure : Different imidazole analogs.

In the above analogs all the substituent's R_1, R_2, R_3, R_4 may be same or different groups as like methyl, ethyl, allyl, benzene, naphthalene, pyridine, furan etc. Further we want to prepare the aromatic substituted analogs in which benzene ring may possess electron donating and withdrawing groups. So we want to prepare all the possible analogs[25-28] and study them. Some examples are as follows.



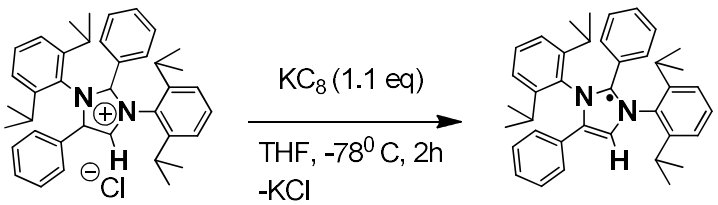
Benzimidazole can be prepared by Hoebrecker[29] method who obtained 2,5-dimethylbenzimidazole by the reduction and dehydration of 2-nitro-4-methylacetanilide.**Scheme7**



o-phenylenediamines react readily with most carboxylic acids to give 2-substituted benzimidazoles, usually in very good yields. The reaction is carried out usually by heating the reactants together on steam bath, under reflux or at an elevated temperature, or some times by heating in a sealed tube. For this purpose various lewis acid catalyst is also used such as $ZrCl_4$, $SnCl_4$, $TiCl_4$, $ZrOCl_2$ and $HFCl_4$.

The most commonly used (Phillip's) method[30] involves the condensation of *o*-diaminobenzenesPhotocyclisation with carboxylic acids or its derivatives, including heating the reagents together in the presence of concentrated hydrochloric acid, this is the most common method for the preparation of wide range of benzimidazoles. We can prepare various 2-substituted benzimidazole derivaties in one step reaction by condensation of o-phenylenediamine and different aromatic acid in the presence of ammonium chloride as catalyst at 80-90 ^oC. The reaction is green and economically viable.2-benzimidazoles can be prepared under microwave irradiation and solvent-free conditions which is catalyzed by alumina, silica gel and zeolite HY over 5-9 min at 160-560 W **Scheme 8**

Imidazole-based radical[4,5] **2** can be prepared with reduction of 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-1H-imidazol-3-ium chloride.



So we are going to synthesize different benzimidazole derivates which can be used to prepare imidazole based radicals. Imidazole based radicals are used to reduce CO_2.

References:

1. (a) I. Omae, *Coord. Chem. Rev.*, 2012, **256**, 1384-1405; (b) I. Omae, *Catal. Today*, 2006, **115**, 33-52, (c) U. S. E. I. Administration, www.eia.gov/oiaf/ieo/index.html
2. (a) M. Mikkelsen, M. Jørgensen and F. C. Krebs, *Energy Environ. Sci.,*2010, **3**, 43. (b) A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer and G. L. Waldrop, *Chem. Rev*., 2013, **113**, 6621.
3. Moret, S.; Dyson, P. J.; Laurenczy, G. *Nat. Commun*. 2014, **5**, 4017. (b) Jeletic, M. S.; Mock, M. T.; Appel, A. M.; Linehan, J. C. *J. Am. Chem. Soc*. 2013, **135**, 11533. (c) Ohtsu, H.; Tanaka, K. *Angew. Chem., Int. Ed*. 2012, **51**, 9792.
4. Aldeco-Perez, E.; Rosenthal, A. J.; Donnadieu, B.; Parameswaran, P.; Frenking, G.; Bertrand, G. *Science* 2009, **326**, 556−559.
5. Bidal, Y. D.; Lesieur, M.; Melaimi, M.; Nahra, F.; Cordes, D. B.; Arachchige, K. S. A.; Slawin, A. M. Z.; Bertrand, G.; Cazin, C. S. J. *Adv. Synth. Catal*.2015, **357**, 3155−3161.
6. Oh, Y.; Hu, X. *Chem. Soc. Rev*. 2013, **42**, 2253−2261.
7. (a) Vincent T. Annibale, Daniel A. Dalessandro, and Datong Song, *J. Am. Chem. Soc* (b) Vincent T. Annibale and Datong Song, *Dalton Trans*., 2016, 45, 32–49; (c) Giorgio Chelucci, and Randolph P. Thummel, *Chem. Rev.* 2002**, 102***,* 3129-3170.
8. a)Arpan Das, Swadhin K. Mandal, *J. Org. Chem*. 2021, **86**, 1246−1252
   b) Sreejyothi, P.; Mandal, S. K.. *Sci*.2020, **11**, 10571−10593.
9. E. C. Riesgo, X. Jin, and R. P. Thummel, *J. Org. Chem.* 1996, **61***,* 3017-30
10. 15.Hossein Sabet-Sarvestani, Mohammad Izadyar, Hossein Eshghi, Nazanin Noroozi-Shad, Mehdi Bakavoli, *Fuel* 2018, **221,** 491–500
11. 14.Hossein Sabet-Sarvestani, Mohammad Izadyar, Hossein Eshghi *Energy* 2017,**134**, 493-503.
12. (a) Vincent T. Annibale and Datong Song, *Dalton Trans*., 2016, 45, 32–49; (b) Giorgio Chelucci, and Randolph P. Thummel, *Chem. Rev.* 2002**, 102***,* 3129-3170.
13. Janes, T.; Osten, K. M.; Pantaleo, A.; Yan, E.; Yang, Y.; Song, D .Chem. Commun.2016,**52**, 4148−4151
14. Ting Ying, Xin Tan, Li Dong, Green Chem., 2019, **21**, 2352-2361.
15. Mallory F.B, Wood C.S, J. Am. Chem. Soc.1964, **86,** 3094-3102.
16. Mallory F.b, Wood C.S, J. Org. Chem.. 1984, **29**, 374-3377.
17. I. Choi, Y. E. Jung, S. J. Yoo, J. Y. Kim, H.-J. Kim, C. Y. Lee and J. H. Jang, J Electrochem Sci Technol 2017, **8**, 61-68.
18. Harish R. Talele, Monik J. Gohil, and Ashutosh V. Bedekar. Bull. Chem. Soc. Jpn. **82**, 1182–1186.
19. M. Courtemanche, M. AndréLégaré, L. Maron, and F. G. Fontaine, *J. Am. Chem. Soc*. 2013, **135**, 9326−9329;
20. S. N. Riduan, Y. Zhang and J. Y. Ying, *Angew. Chem. Int. Ed*. 2009, **48**, 3322 –3325.
21. Heilbronner, E.; Fróhlicher, U.; Plattner, PI. A. Helo. Chim. Acta

1949, **32**, 2479.
22. Yamashita, S. Bull. Chem. Soc. Jpn. 1961, 34, 972.
23.Martinho, K. A. Top. Curr. Chem. 1980, 88,89.

24.G. Fiorani, W. Guo and A. W. Kleij*, Green Chem*., 2014, **16**, 1-3.
25. Villar, J. M.; Suárez, J.; Varela, J. A.; Saá, C. *Org. Lett.* 2017, **19** (7), 1702–1705.

26. Lim, C.-H.; Ilic, S.; Alherz, A.; Worrell, B. T.; Bacon, S. S.; Hynes, J. T.; Glusac, K. D.; Musgrave, C. B. *J. Am. Chem. Soc.* 2018, **141** (1), 272–280.

27. Zhu, X.-Q.; Zhang, M.-T.; Yu, A.; Wang, C.-H.; Cheng, J.-P. *J. Am. Chem. Soc.* 2008, **130** (8), 2501–2516.

28. Ilic, S.; Alherz, A.; Musgrave, C. B.; Glusac, K. D. *Chem. Commun.* 2019, **55** (39), 5583–5586.

29. F. Hoebrecker, Ber. **5** (1872) 920–926.

30. M. Phillip, *J. Chem. Soc. C*. (1971) 1143–1145.

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